

***In situ* SXS Study of Electrodeposited Bi on Au(111) Catalytically Active for Oxygen Reduction**

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Introduction: A prototypical system for studying electrodeposited metal monolayers, referred to as underpotential deposition (UPD) is the Bi on the Au(111) system. The UPD Bi adlayer can alter the electrocatalytic activity with regard to oxygen/hydrogen peroxide reduction, which makes this system particularly interesting. Ordered Bi adlayers form on Au(111), as determined by x-ray and scanning probe techniques^{1,2} which exhibits unusual catalytic activity. However, the relationship between the detailed structure of the Bi adlayer and the reactivity of oxygen and hydrogen peroxide has not been determined during the course of oxygen reduction. In this study, the structure of the UPD Bi monolayer during electrocatalytic oxygen reduction was investigated using *in situ* surface X-ray scattering techniques.

Methods and Materials: A single crystal Au(111) electrode was prepared by flame annealing followed by quenching with Milli-Q water. A 0.1 M HClO₄ solution containing 2.5 mM Bi₂O₃ was used as the electrolyte and all potentials are referenced with respect to a Ag/AgCl electrode. The electrochemical cell was constructed from Kel-F and was closed by using a thin Prolene film. N₂ and/or O₂ gases were brought into the cell through the Prolene film.

Results and Discussions: The potential dependent x-ray scattered intensity was measured at the lowest order in-plane reflection from the (2x2)-Bi adlayer for several O₂ partial pressures (Fig. 1). In from the (2x2) phase was observed between the absence of oxygen, the scattered intensity 0.18 and 0.25 V. With 10% O₂, the peak width was broadened and the peak potential was shifted. Above 10% of O₂, the peak intensity decreased as the O₂ partial pressure increased. At 50% of O₂, the scattering intensity from (2x2)-Bi layer could not be observed. The O₂ pressure dependence of the scattered x-ray intensity was also investigated for the (px√3)-Bi phase (not shown). The (px√3) structure is active only for two-electron O₂ reduction and exists at a partial pressure of 50% O₂. A more open (2x2) structure is active for a four-electron O₂ reduction and is less stable in the presence of O₂ than the more compact and less active (px√3) phase. The origin of the catalytic effect of Bi will be analyzed in view of these findings.

References:

1. C. Chen, K. Kepler, A. Gewirth, B. Ocko, and J. Wang, "Electrodeposited Bismuth Monolayers on Au(111) Electrodes: Comparison of Surface X-ray Scattering Tunneling Microscopy, and Atomic Force Microscopy Lattice Structure", **97**, 7290, J. Phys. Chem., 1993.
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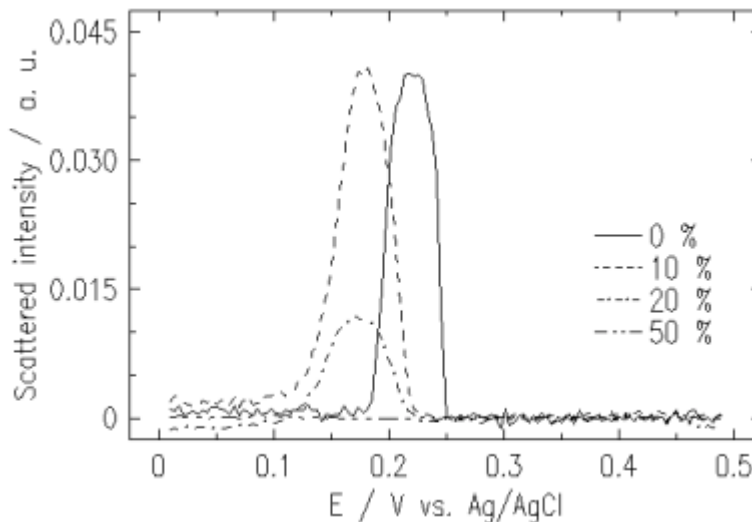


Figure 1 O₂ partial pressure dependence of the scattered intensity from the (2x2)-Bi layer.